

# Atrazine Chlorination Transformation Products Under Drinking Water Distribution System Conditions

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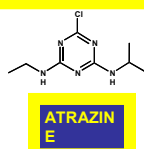
## Abstract

Chlorination is a commonly-used disinfectant step in drinking water treatment. Should free chlorine be added to water used as a drinking water source, it is widely understood that many biological species in the water along with dissolved organic and inorganic chemicals will react with the chlorine. Reaction with biological species can result in beneficial disinfection of the water, while reaction with the chemicals can produce detrimental by-products. If pesticides are present, whether from agricultural runoff or an accidental spill, they might undergo reactions with chlorine. This investigation focuses on atrazine, a widely applied herbicide (76 million pounds annually), which is but one of many potential chemicals of concern (U.S. EPA-IREDD, 2003). It has been reported that atrazine entering a drinking water treatment plant is essentially not transformed by chlorination. However, more recent concerns about pesticides focus not on what comes out of the plant, as required by the amended Safe Drinking Water Act, but what reaches the tap. The Food Quality Protection Act also necessitates consideration of all potential routes of pesticide exposure including drinking water routes. The U.S. EPA currently regulates atrazine at 3 ppb but is considering regulating the triazine family (U.S. EPA-revised IRED, 2003).

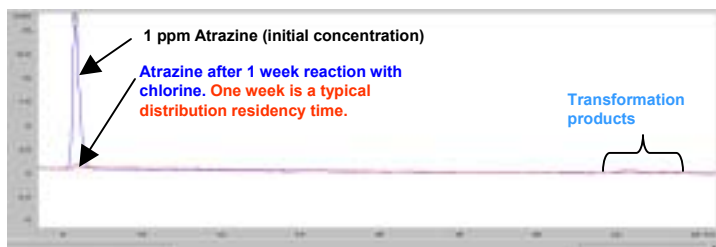
Residency times in distribution systems are usually in days as opposed to minutes inside plants; this may allow sufficient time for the atrazine to be transformed by chlorination into unknown species with unknown toxicities. Hence, there is a need to more completely study atrazine chlorination. This study aims to address three important issues in this regard. First, the proper chemical conditions in which atrazine transforms need to be determined. Second, any potential transformation products need to be identified. Third, the mechanistic pathways for these transformation products will have to be proposed. This study will investigate chlorination of atrazine in laboratory water buffered to several pH values ranging from 5.5 to 8.5. Gas chromatography/mass spectrometry (GC/MS) and high performance liquid chromatography with UV and MS detection (HPLC/UV and HPLC/MS) will be used to detect any transformation products.

**STUDY DESIGN: PHASE 1-Transformation Product Observation (complete), PHASE 2-Transformation Product Identification (in progress), PHASE 3-Mechanistic Pathway Postulation**

## Phase 1 Chlorination of Atrazine



Observations: The reaction is dependent on pH and time. The analytical quantification depends on the methodology employed.



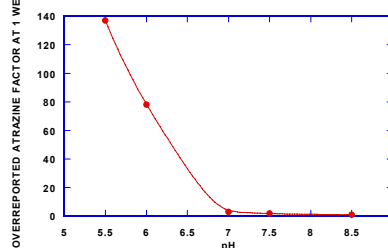
Atrazine and Chlorination Transformation Products by HPLC/UV

**Atrazine quantification.** Table 1 shows atrazine loss at 1 week determined by GC/MS and HPLC/UV. Table 1 also shows the effect of chlorine quenching agents which are necessary for the analysis. Note: EPA method 525.2, a compliance monitoring method for determining atrazine, uses both GC/MS and sodium sulfite quenching.

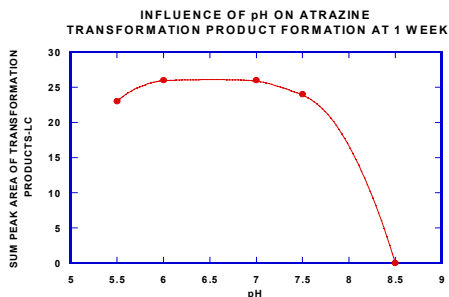
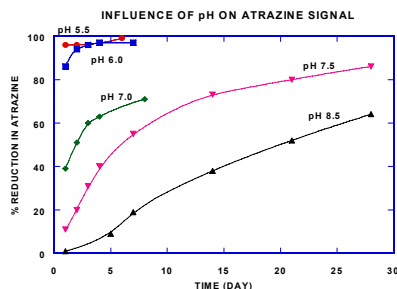
Table 1

pH	% transformation by GC/MS with Ammonium Chloride quench	% transformation by HPLC/UV with Ammonium Chloride quench	% transformation by HPLC/UV with Sodium Sulfite quench	The factor by which atrazine is overreported when sodium sulfite is used (as in EPA Method 525.2).
5.5	43	99	5	136
6.0	50	97	8	76
7.0	16	71	3	2.24
7.5	6	55	15	0.80
8.5	30	19	13	0.0076

EFFECT OF pH ON THE ATRAZINE OVERREPORTED FACTOR



**Effect of pH and time.** The following figures are based on HPLC results using ammonium chloride as the dechlorinating agent.



## Three Implications

The data suggest two particularly meaningful implications for the regulation, monitoring, and the scientific understanding of atrazine:

- 1) If the usual approach of atrazine analysis is employed, method 525.2, for chlorinated waters, the atrazine concentration can be OVER-reported by up to nearly 13600 % (Table 1). This would seem to have certain regulatory implications for human exposure to atrazine contaminated water.
- 2) The transformation byproducts, because they may be chlorinated, may be more toxic than the parent atrazine. This may affect the risk analysis of consuming atrazine contaminated water. This may ultimately affect the regulation of atrazine because future reregistration of pesticides may have to account for the toxicities of not only the parent pesticide but also the transformation products.
- 3) When performing transformation work the dechlorinating agent must be compatible with analysis of the product, not just the parent pesticide.

References:  
U.S. EPA-IREDD, "October 31, 2003 Revised Atrazine IRED," <http://www.epa.gov/oppsrrd1/reregistration/atrazine/atrazineadd.pdf>  
Safe Drinking Water Act (SDWA) <http://www4.law.cornell.edu/uscode/42/300f.html>  
Food Quality Protection Act (FQPA) <http://www.epa.gov/oppead1/fqpa/gpogate.pdf>